Light Hydrocarbons in Recent Texas Continental Shelf and Slope Sediments

BERNIE B. BERNARD, JAMES M. BROOKS, AND WILLIAM M. SACKETT

Department of Oceanography, Texas A&M University, College Station, Texas 77843

The distributions of the concentrations of methane, ethene, ethane, propene, and propane in twelve 1-to 2-m-long gravity cores for two transects from nearshore to midslope off the southwest Texas Gulf Coast are reported. Methane profiles exhibit maxima in the top 40 cm of sediment on the shelf, in contrast to downward increasing gradients in the slope region. Nearshore surface methane concentrations ranging from 50 to 400 μl (normal temperature and pressure) per liter pore water are apparently due to microbial production in sulfate-free microenvironments such as fecal pellets in a near-seawater sulfate environment. A decrease in sediment methane levels to less than 5 μl/l pore water in downslope sediments is attributed to reduced microbial activity due to lower organic contents and temperatures. Profiles of the saturated and unsaturated C_2 and C_3 hydrocarbons suggest that these gases are also microbially produced.

INTRODUCTION

Since the early report of gases in marine sediments by *Emery and Hoggan* [1958], several investigators have published concentrations of methane and other gases in near-surface marine sediments [*Reeburgh*, 1969, 1976; *Reeburgh and Heggie*, 1974; *Whelan*, 1974; *Martens and Berner*, 1974, 1977; *Barnes and Goldberg*, 1976]. These studies are all concerned with anoxic marine sediments such as are found in deltas, estuaries, marshes, and marine basins. Methane exists in these sediments as a result of microbial production from organic substrates and/or CO_2. Since large quantities of methane (several milliliters per liter interstitial water) have only been observed in marine sediments below the depth of sulfate depletion and all known methanogenic bacteria are obligate anaerobes [*Toerien and Hattingh*, 1969], it has been accepted that methane is microbially produced only in the absence of dissolved sulfate below the anaerobic sulfate reduction zone [*Claypool and Kaplan*, 1974]. *Martens and Berner* [1974] suggested that methane could be produced above this zone within organic-rich microenvironments such as decaying organisms or shell fragments. *Barnes and Goldberg* [1976] reported methane concentration profiles from anoxic Santa Barbara Basin sediments which indicated that methane was actively consumed by the bacterial population of the sulfate-reducing zone. They suggested that methane generation and sulfate reduction are not mutually exclusive processes but rather that low methane levels in sulfate-reducing sediments represent a balance between production by methanogenic bacteria and consumption by sulfate reducers. *Martens and Berner* [1977] recently concluded that methane is most likely produced only in the absence of bacterial sulfate reduction, and upon diffusing upward it is consumed by sulfate-reducing bacteria. Reported here are measurements of methane in lower Texas continental shelf and slope sediments of the Gulf of Mexico. The top few meters of the sediments studied are only mildly reducing, having interstitial sulfate concentrations similar to those of seawater. Dissolved gas profiles indicate that methane is microbially produced at the greatest rates in the top several centimeters of these shelf and slope sediments.

ANALYTICAL METHODS

Sediment samples were obtained by using standard gravity coring techniques. Upon retrieval the sediment, contained in a plastic liner, was removed from the core barrel and sectioned at specific depths. Five-centimeter sections were immediately extruded into 0.5-l containers holding 125 ml of sodium-azide-poisoned hydrocarbon-free seawater. The containers were capped, and the headspaces flushed with helium or nitrogen through septa in the lids. The hydrocarbon gases dissolved in the interstitial water were equilibrated with the gas phase by agitation for 5 min with a high-speed shaker. The shaker also dispersed the sodium azide throughout the sediment to inhibit microbial activity. The headspace gases were then analyzed, or the containers were inverted to form liquid seals around the lids and stored in darkness at near-freezing temperatures until analysis.

The system for analysis of the light hydrocarbons is shown schematically in Figure 1. Trap A contains activated charcoal maintained at liquid nitrogen temperature for removal of hydrocarbon impurities in the purge helium stream. The system is flushed by opening all valves and heating trap B to ~90°C with a boiling water bath. Trap B contains Porapak Q as a substrate to collect the hydrocarbons. Liquid nitrogen is placed around the trap, and valve C is closed before the container is coupled to the system by inserting 20-gauge needles into the septa (outflow line first). Helium enters the sample container through valve D, purges the headspace gases through an anhydrous magnesium perchlorate drying tube, and carries the light hydrocarbons into trap B, where they are quantitatively collected.

The flush rate is adjusted by valve D to 1 l/min so that the hydrocarbons in the 0.2-l headspace are quantitatively removed in 2 min. The trap is then isolated by closing valves F and G, and the container removed from the system. The trap is then heated and injected into the carrier stream by a pneumatic slide valve, and the hydrocarbons are separated on a 3-m, 1.5-mm-ID Porapak Q column thermostated at 60°C. A flame ionization detector (HP 5710A gas chromatograph) is used in conjunction with an electronic integrator (HP 3380) for the analysis of hydrocarbon concentrations. A typical chromatogram showing separation of the gases is shown in Figure 2.

Because of the solubility differences of the light hydrocarbons in seawater the partition coefficients between the water-sediment mixture and the headspace vary for each hydrocarbon. Partition coefficients for the individual hydrocarbons were determined by repeated equilibrations of samples after replacement of the headspace gas with helium. After purging,

Paper number 8C0204.
0148-0227/78/088C-0204$01.00

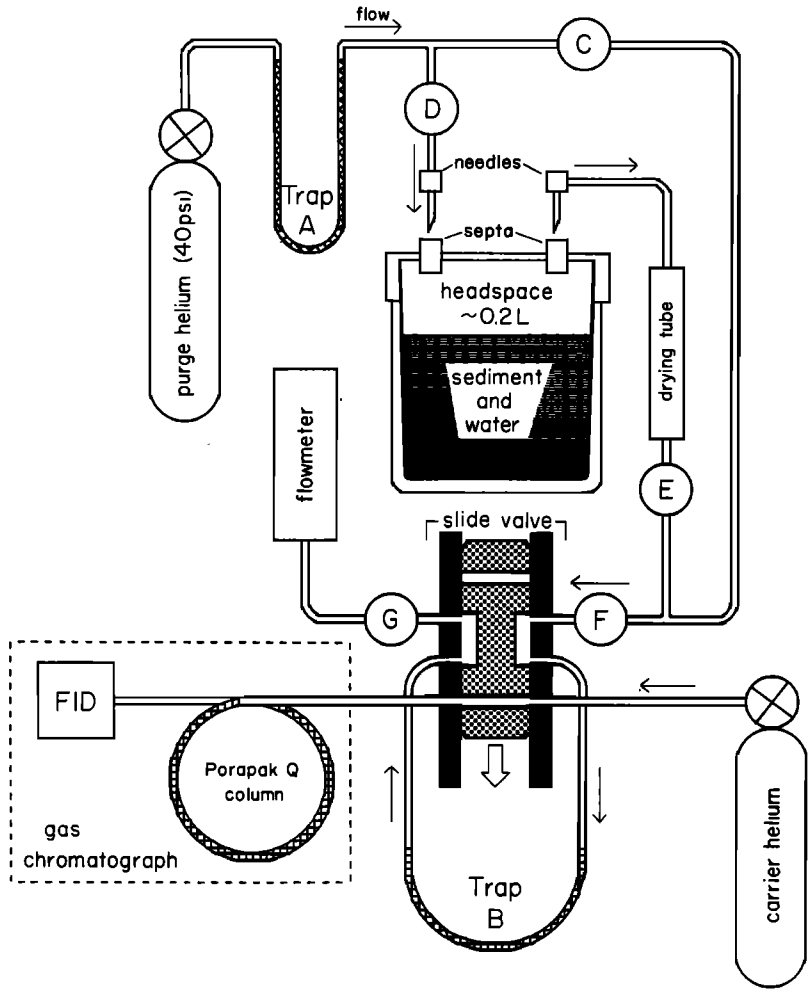


Fig. 1. Schematic of the system used for analysis of sediment light hydrocarbons.

the sample container was reagitated, and the analysis procedure repeated. The individual partition coefficients were calculated by

$$K_i = 1 - (X_2/X_1)_i \quad (1)$$

where K is the partition coefficient for a particular hydrocarbon and $(X_2/X_1)_i$ is the ratio of the detector response generated by component i from the first (X_1) and second (X_2) equilibrations. These partition coefficients represent the fraction of total gas in a sample container that is present in the gas phase after an equilibration. Since at least 80% of every light hydrocarbon gas is removed from the sediment by each equilibration, simply summing the response from the first two equilibrations would represent at least 96% recovery of each gas from the sediment samples. Since coefficients for a group of cores taken and analyzed under similar conditions are quite repetitive, it is faster and more accurate to establish standard partition coefficients of each gas in a group of core samples by performing second equilibrations only on selected samples. The total response of a gas in a sample (T_i) can then be calculated by using

$$T_i = (X_1/K)_i \quad (2)$$

After a volume of a standard gas mixture is trapped and injected into the gas chromatograph for calibration, concentrations of each gas can be calculated by

$$C_i = (C_{std}/X_{std})_i \times (V_{std}/V_{mud}) \times T_i \quad (3)$$

where gas concentration C_i is in microliters per liter wet sediment, C_{std} is the concentration of component i in a standard gas mixture in parts per million, X_{std} represents the detector response generated by standard component i, V_{std} is the volume of standard gas in milliliters, and V_{mud} is the volume in milliliters of sediment placed in the sampling container.

As an experimental verification of the analytical procedures a sediment sample was equilibrated and purged five times to remove all measurable light hydrocarbons. A 20-cm³ sample of standard gas containing quantities of light hydrocarbons in the range of those typically measured in continental shelf sediment samples was injected into the container. The container was then agitated to equilibrate the hydrocarbons, and headspace gases were measured as was previously outlined. After pur-

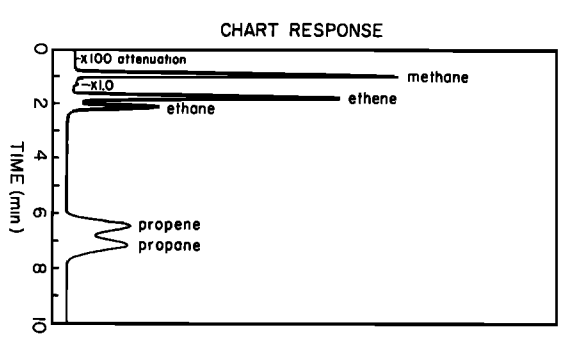


Fig. 2. Chromatogram of sediment light hydrocarbons.

TABLE 1. Gas Partitioning Experiment

	Methane	Ethene	Ethane	Propene	Propane
Nanoliters of gas injected	380	16	17	15	18
Response, first equilibration (X_1)	619.8	51.57	60.51	72.09	91.89
Response, second equilibration (X_2)	37.25	7.425	4.039	9.313	3.966
Calculated partition coefficient (K)	0.940	0.856	0.933	0.871	0.957
Calculated total units in sample (T)	659.4	60.2	64.9	82.8	96.0
Response, calibration standard (X_{std})	666.5	59.2	65.3	81.7	96.5
Percent deviation of T from X_{std}	−1.1	1.7	−0.6	1.3	−0.5

Symbols are explained in text.

ging, the container was reequilibrated, and the new headspace gases were measured. The data generated by the experiment are presented in Table 1. For each hydrocarbon gas the table lists the number of nanoliters contained in 20 cm³ of the standard mixture, the integrator units generated from the first and second equilibrations of the container, and the resulting partition coefficients. Also tabulated are the integrator units measured from direct analysis of the hydrocarbons in 20 cm³ of the standard gas (these represent the total units which were injected into the container) and the total units in the sample calculated by (2). Percentage deviations of the calculated and measured values show that there was less than a 2% error for every hydrocarbon by calculating concentrations from partition coefficients. Therefore if consistent partition coefficients are established for a large group of samples, most of the samples analyzed need to be equilibrated only once.

Average partition coefficients calculated from two large groups of sediment samples taken from the Texas continental shelf and slope are presented in Table 2. Both groups were stored in a refrigerator, but group A was warmed to room temperature (20°C) before analysis, whereas group B was heated to about 40°C in a hot-water bath. The gas solubilities in 20°C distilled water calculated from the data of *McAuliffe* [1966] are also tabulated for comparison. The solubilities of most of these gases in seawater are not accurately known but should follow the same trend as is followed in distilled water. Partition coefficients are a function of the solubilities of gases, which in turn depend on temperature. The coefficients listed in Table 2 reflect the relative gas solubilities, decreasing with increasing solubility, and so on. Group B partition coefficients were noticeably higher than those of group A, indicating the negative effect of higher temperature on gas solubilities. Higher partition coefficients decrease the chance of error in the calculation of total gas in the samples because relatively more gas is removed from the sample during the first equilibration, so warming the samples to 40°C is now the preferred procedure.

For each section of sediment sampled for light hydrocarbons an adjacent sample of sediment was collected, weighed, freeze-dried, and reweighed for the determination of weight percent interstitial water. From this percentage, porosity can be calculated, and concentrations of light hydrocarbons are reported per liter interstitial water rather than wet sediment.

For measuring methane concentrations in excess of saturation at 1-atm pressure, such as are typically found in sulfate-free, reducing sediments, our sampling method is inferior to the so-called in situ pore water samplers developed by other investigators, because of the possibility of outgassing during core retrieval. However, in situ samplers cannot presently sample sufficient pore water for precise determinations of light hydrocarbons other than methane. The sediment depth which can be reached and the sampling intervals are also somewhat limited by the in situ technique. Concentrations of hydrocarbon gas existing in the top few meters of the Texas continental shelf and slope sediments are far below saturation, so that the escape of gas during handling by our sampling method is driven only by the processes of molecular diffusion from the core material. The time period that the core material is exposed to conditions causing loss of gas due to outward diffusion after extrusion is generally less than 1 min. The depth within the core section to which significant gas loss occurs during this time can be estimated by using a diffusion coefficient of 2×10^{-6} cm²/s [*Martens and Berner*, 1977] to be about 0.1 mm. In effect then, in 1 min, diffusive processes skim the outer 0.1 mm from the surface of the exposed core section, introducing a maximum reduction of 1% in the total gas content of a sample.

LIGHT HYDROCARBON AND SULFATE DATA

Light hydrocarbon concentrations measured in sediments taken at 12 stations on the Texas continental shelf and slope are listed in Table 3. The stations are located on two transects progressing seaward from the shoreline (Figure 3). Methane concentrations are reported as microliters (normal temperature and pressure (NTP)) per liter interstitial water, and the other gases as nanoliters (NTP) per liter interstitial water. Estimated errors for dissolved gas determinations are less than ±3%. Sulfate was determined on interstitial water samples by barium sulfate gravimetry [*Vogel*, 1968] at selected depths in cores taken at stations 1–7. These samples were taken immediately above core sections for light hydrocarbons, and millimolar sulfate concentrations are listed adjacent to corresponding light hydrocarbon sampling intervals in Table 3.

TABLE 2. Partition Coefficients of Two Groups of Samples

	Methane	Ethene	Ethane	Propene	Propane
Group A (20°C)	0.944	0.840	0.897	0.835	0.950
Group B (40°C)	0.955	0.848	0.919	0.902	0.960
Solubility at 20°C, * ml/l	34	105	45	107	32

*Calculated from data of *McAuliffe* [1966].

TABLE 3. Light Hydrocarbon and Sulfate Concentrations in Texas Shelf and Slope Sediments

Depth, cm	Methane, μl/l	Ethene, nl/l	Ethane, nl/l	Propene, nl/l	Propane, nl/l	Sulfate, mM
			Coring Station 1			
5–10	393	154	87	77	51	26.9
15–20	52.1	147	87	98	57	26.8
25–30	26.0	139	89	102	55	
35–40	9.1	130	110	102	68	
45–50	14.7	211	117	140	79	25.5
65–70	7.5	179	109	117	68	
85–90	6.8	177	134	129	81	25.5
105–110	7.6	139	92	104	60	25.5
			Coring Station 2			
5–10	278	114	43	59	46	30.2
15–20	76.0	87	56	70	43	
25–30	19.6	107	56	70	47	
35–40	15.5	126	72	82	46	28.3
45–50	16.5	114	60	74	37	
65–70	18.2	94	60	68	37	27.0
85–90	19.7	68	40	55	29	
105–110	22.8	126	66	85	37	
125–130	30.8	85	57	72	42	26.9
145–150	19.3	176	95	122	57	
165–170	19.5	149	68	104	43	24.7
			Coring Station 3			
5–10	77.6	71	33	50	36	27.4
15–20	28.5	82	48	60	30	
25–30	35.4	111	55	66	34	
35–40	19.4	137	58	84	29	27.6
45–50	15.4	102	52	68	23	
65–70	17.6	94	46	76	27	
85–90	17.2	91	51	48	30	26.6
105–110	15.8	93	55	67	28	
125–130	15.7	75	48	58	25	25.7
145–150	15.7	84	55	67	25	
165–170	12.7	140	59	91	27	24.7
			Coring Station 4			
5–10	75.5	60	24	37	34	28.7
15–20	37.7	61	32	42	35	
25–30	6.72	89	37	49	36	26.3
35–40	3.23	80	36	47	37	
45–50	2.32	56	27	43	33	26.3
65–70	2.57	80	37	52	36	
85–90	2.65	84	40	63	35	25.8
105–110	3.13	61	35	52	35	
125–130	3.18	74	40	52	32	25.2
			Coring Station 5			
5–10	6.60	75	26	29	21	
15–20	2.39	55	24	26	16	
25–30	2.54	58	28	34	19	
35–40	2.79	59	28	32	18	25.3
45–50	3.25	67	29	35	19	
65–70	3.67	96	35	43	23	
85–90	3.87	103	36	40	21	26.2
105–110	3.74	30	23	33	17	
125–130	4.00	52	26	30	17	25.5
145–150	4.34	54	30	35	22	
165–170	3.86	61	25	33	17	22.2
			Coring Station 6			
5–10	1.05	60	23	33	26	26.9
15–20	1.23	64	22	34	33	
25–30	1.59	63	24	30	25	
35–40	1.79	90	25	39	26	26.5
45–50	2.08	96	27	36	22	
65–70	2.40	81	29	34	29	
85–90	2.64	82	26	34	27	26.3
105–110	2.96	78	29	31	26	
125–130	3.08	83	25	31	26	26.2
145–150	3.40	55	23	29	25	26.1

TABLE 3. (Continued)

Depth, cm	Methane, μl/l	Ethene, nl/l	Ethane, nl/l	Propene, nl/l	Propane, nl/l	Sulfate, mM
			Coring Station 7			
5–10	0.44	45	13	34	20	27.6
15–20	0.89	64	15	32	26	
25–30	1.38	80	19	32	27	
35–40	1.78	177	20	32	30	
45–50	2.00	64	20	33	32	27.1
65–70	2.47	51	17	28	25	
95–100	2.93	87	20	32	33	26.3
125–130	3.43	49	19	25	29	25.9
165–170	4.13	52	18	30	31	25.7
			Coring Station 8			
5–10	104	107	39	23	32	
15–20	232	159	55	53	41	
25–30	258	102	37	52	42	
35–40	212	100	31	43	35	
45–50	194	94	31	43	42	
65–70	54.9	75	25	32	32	
85–90	25.7	129	40	60	62	
105–110	19.4	88	29	39	29	
			Coring Station 9			
5–10	171	56	14	11	11	
15–20	211	110	33	36	31	
25–30	70.7	99	37	44	37	
35–40	17.9	74	29	36	30	
45–50	17.0	86	31	47	37	
65–70	21.1	80	27	39	39	
85–90	20.0	107	32	49	38	
105–110	20.1					
125–130	16.9	88	19	24	16	
			Coring Station 10			
5–10	10.1	96	25	31	25	
15–20	13.6	123	36	42	46	
25–30	13.1	99	36	49	41	
35–40	12.3	65	26	28	29	
45–50	13.1	71	25	35	33	
65–70	20.0	101	32	58	35	
85–90	14.8	123	30	53	35	
105–110	16.6	68	20	35	31	
			Coring Station 11			
5–10	3.22	52	12	15	32	
15–20	2.65	77	22	28	30	
25–30	2.92	65	20	28	24	
35–40	2.95	71	25	37	27	
45–50						
65–70	4.15	70	19	36	34	
85–90	4.96	100	27	47	37	
105–110	6.01	80	26	41	27	
125–130	5.74	82	25	43	40	
			Coring Station 12			
5–10	2.77	60	12	15	11	
15–20	1.58	46	14	23	31	
25–30	1.64	60	17	26	20	
35–40	2.05	68	18	34	28	
45–50	1.76	52	15	24	25	
65–70	1.96	64	20	33	32	
85–90	2.59	60	17	28	25	
105–110	2.85	65	20	40	41	

METHANE PROFILES

Interstitial methane concentrations in sediments along the two transects are plotted against sediment depth in Figures 4 and 5. Stations 1–7 (transect I) are shown in Figure 4, and Figure 5 contains stations 8–12 (transect II). Concentration profiles are positioned on the figures relative to the sea floor depth where the cores were taken (dashed lines represent sea floor contours). Water depths and distances from shore to the stations are written along the axes of the profiles. Concentration and sediment depth scales are identical in all profiles. The profiles are plotted in this manner to illustrate the influence of

water depth on sediment methane concentrations. Methane levels are generally higher at nearshore stations and show a very discernable maximum within the top 30–40 cm of sediment. These profiles indicate that methane is not diffusing upward from deeper sulfate-free zones, since there is not an increasing methane gradient with depth. Interstitial sulfate in the top few meters of these shelf sediments has not been significantly depleted (Table 3), and the depth of sulfate disappearance in this area of the South Texas shelf occurs at least several meters below the sediment surface, so methane should theoretically not be produced in the surface sulfate-rich sediments.

Water column methane concentrations have been measured monthly during the last 2 years in the South Texas shelf area [*Sackett et al.*, 1977], and while methane maxima in near-bottom waters have been consistently observed in some areas, few concentrations above 0.4 μl/l have been observed. Therefore methane concentrations in surface sediments as high as several hundred microliters per liter cannot be a result of diffusion downward from the water column but result rather from in situ production.

That microbial populations are most extensive and physiologically versatile in the top layers of sediment has been known for some time [*Certes*, 1884; *Russell*, 1892; *Drew*, 1912; *Lloyd*, 1931; *Reuszer*, 1933; *Zobell and Anderson*, 1936; *Kaplan and Rittenburg*, 1963]. Wherever vertical profiles of bacterial populations have been examined in marine sediments, a progressive decrease in the bacterial populations with increasing sediment depth has been observed [*Zobell*, 1946]. The decrease is most rapid in the top few centimeters of sediment and generally slows, becoming sporadic with increasing depth [*Zobell*, 1942]. The vertical distribution of bacteria in sediments can be directly correlated with available organic matter and nutrient material. Much of the organic matter of marine sediments consists of material which is fairly refractory to bacterial decomposition, so changes in total organic matter with sediment depth due to microbial activity are seldom observable. The surface sediment is subject to a constant rain of organic detritus, however, including the more labile material which is rapidly consumed by bacteria before burial. As available organic matter and nutrients disappear with depth in the sediment, bacterial populations decrease.

There are obvious similarities between vertical bacterial distributions and the vertical methane profiles of nearshore stations illustrated in Figures 4 and 5. The two figures suggest that the methanogenic bacteria exist in large numbers near the sediment surface and are possibly active inside small microreducing environments in the sediment where reduction of ambient sulfate has occurred. These microniches could take the form of fecal pellets, decaying organic matter, shell fragments, or flocculent clay particules. Methane produced in the microenvironments apparently diffuses into the surrounding sediment, where it is oxidized by sulfate-reducing bacteria [*Barnes and Goldberg*, 1976; *Martens and Berner*, 1977], and upward into the overlying bottom water, where it is removed by advection.

The shelf stations taken along transects I and II (Figures 4 and 5) are at similar water depths and distances from shore, so if only these factors affect methane concentrations, corresponding profiles in the two figures should ideally be identical. This is not the case, since the profiles along transect I show methane increasing upward to the 5- to 10-cm interval, whereas the profiles of transect II indicate a methane maximum at the 25- to 30-cm interval (concentrations in the 0- to 5-cm interval are unknown). The lack of uniformity in the distribution of bacteria among the various sediment types observed on the Texas shelf can explain these differences. Bacterial distributions are intimately associated with the physical consistency and organic content of the sedimentary deposits. In some areas, submarine topography has a greater influence on the median particle size and organic content of sediments than the depth of water or distance from shore. *Zobell* [1946] states that bacterial populations are more closely related to the character of the sediments than to their distance from land, and, as a rule, sand contains fewer bacteria than sediments consisting of smaller particles. The greater abundance of bacteria found in finer sediments is attributed primarily to a higher organic content. Although several other interrelated factors are involved, the bacteria in the shelf sediments of transect II may prefer the sediment type and organic content of the deposits at 25-cm depth rather than the sediment surface.

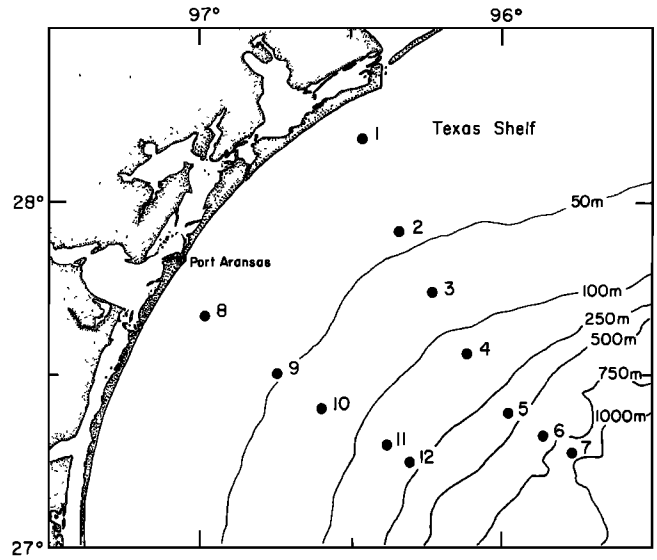
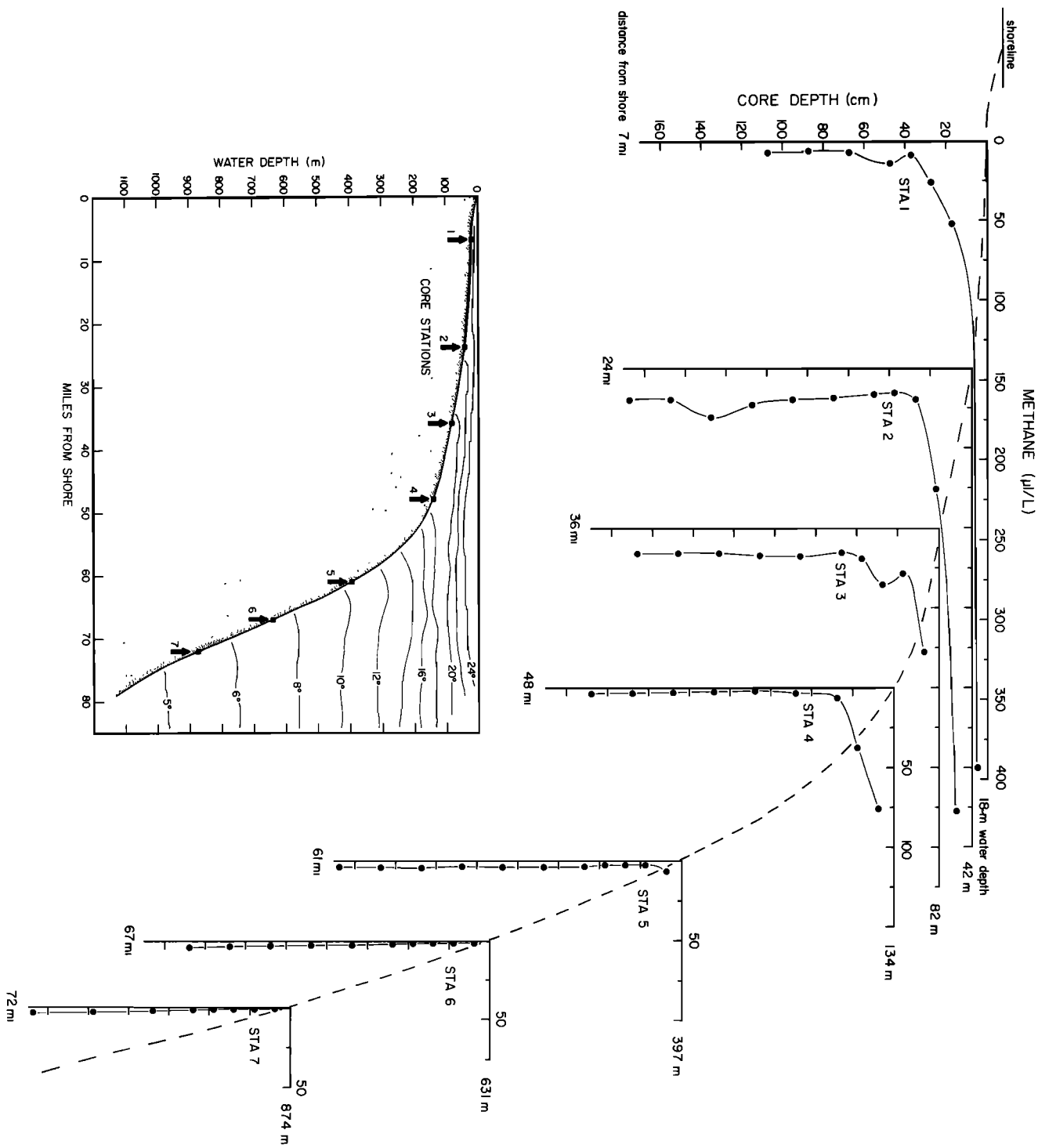


Fig. 3. Locations of cores taken on the Texas continental shelf and slope.

Figures 4 and 5 also illustrate the disappearance of the surface methane maximum in cores taken progressively further offshore. In Figure 4 the methane maximum decreases significantly at station 4, is barely visible at station 5, and disappears at stations 6 and 7. The decrease of the near-surface methane with increasing distance from shore can be explained by changes in microbial activity rather than changes in populations. Bacterial numbers generally decrease outward on the Texas continental shelf (J. R. Schwarz, personal communication, 1977), although millions of bacteria per gram of sediment are still found in sediments several thousands of meters deep, so the observed decrease of the methane maximum cannot be explained on the basis of bacterial numbers alone. In some areas, there are actually more bacteria in sediments from deep water, where the temperatures are 3°–7°C, than in those from shallow water, where bottom temperatures are considerably higher [*Zobell and Anderson*, 1936]. The optimum temperatures for the multiplication of marine bacteria range from 20° to 25°C, but while lower temperatures retard reproduction, survival of the bacteria is prolonged.

Fig. 4. (Opposite) Vertical profiles of interstitial methane (microliters per liter pore water) along transect I, positioned on the sea floor contour. Inset shows the general temperature structure of the area in spring.


METHANE (µl/L)
shoreline
18-m water depth
42 m
CORE DEPTH (cm)
distance from shore 7 mi
STA 1
24 mi
STA 2
36 mi
STA 3
48 mi
STA 4
61 mi
STA 5
67 mi
STA 6
72 mi
STA 7
82 m
134 m
397 m
631 m
874 m
WATER DEPTH (m)
MILES FROM SHORE
CORE STATIONS
24°
20°
16°
12°
10°
8°
6°
5°

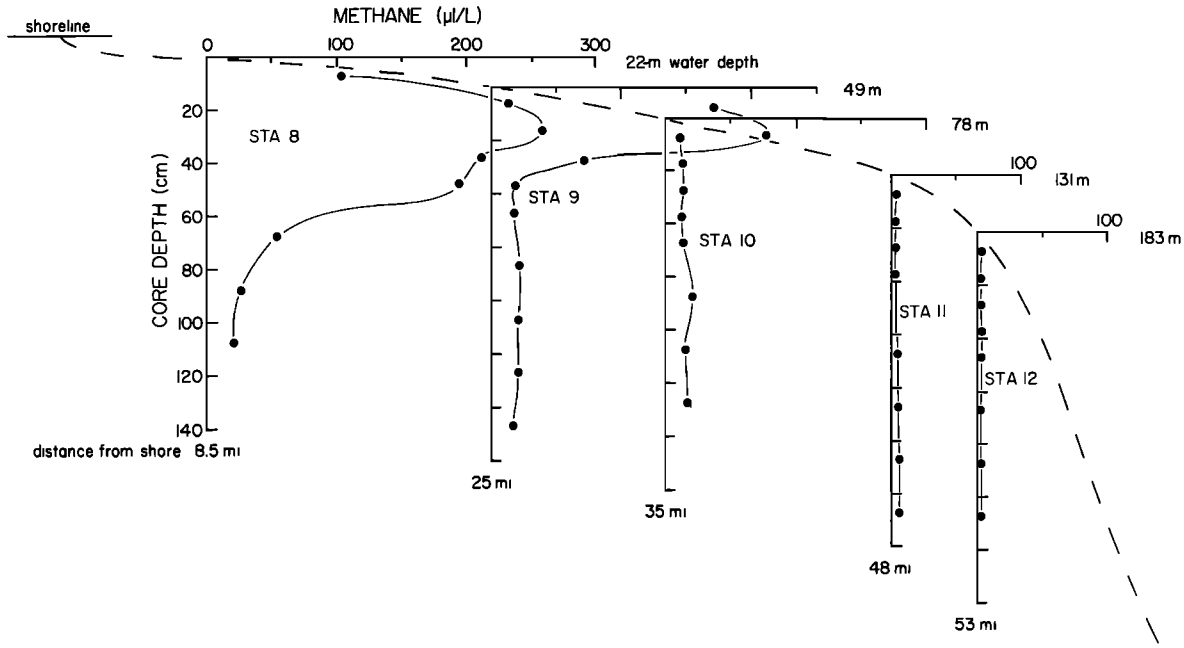


Fig. 5. Vertical profiles of interstitial methane (microliters per liter pore water) along transect II, positioned on the sea floor contour.

General water temperature contours at the study area are shown in the inset in Figure 4. These temperatures are representative of late spring but do not change significantly below 200 m throughout the year. Stations are marked on the inset, and surface methane concentrations correlate well with the temperature contours. Temperatures below ~15°C beyond the shelf break must inhibit microbial activity and methane production to the extent that methane diffuses out of the sediment before it can accumulate as it does nearer shore. This conclusion implies that surface methane production in Texas shelf sediments might be seasonally influenced. Low temperatures nearshore in winter (~12°C) could inhibit microbial activity and slow methane production. Warming of the sediments in the spring and summer, enhanced by increased detrital input from phytoplankton blooms and runoff, might accelerate methane production in the microenvironments, causing annual methane oscillations at the tops of nearshore sediments.

Sediment methane concentrations below the surface maxima also vary with distance from shore. On the upper continental shelf, methane levels in this layer generally ranged from 15 to 20 μl/l pore water and showed no trends with depth in the upper 1.5 m of sediment. In the slope region, concentrations decreased progressively in an offshore direction to less than 5 μl methane per liter pore water, and downward increasing gradients were observed in the sediment. Higher methane concentrations in the shelf region are attributed to greater microbial activity in the sediments as a result of higher temperatures and greater amounts of available organic material in those sediments than in sediments deposited further offshore. The downward increasing methane gradients observed on the slope are apparently the result of an equilibrium between diminished methane production within microreducing environments, methane oxidation by sulfate-reducing bacteria, and diffusion of methane from the top layer of sediment into

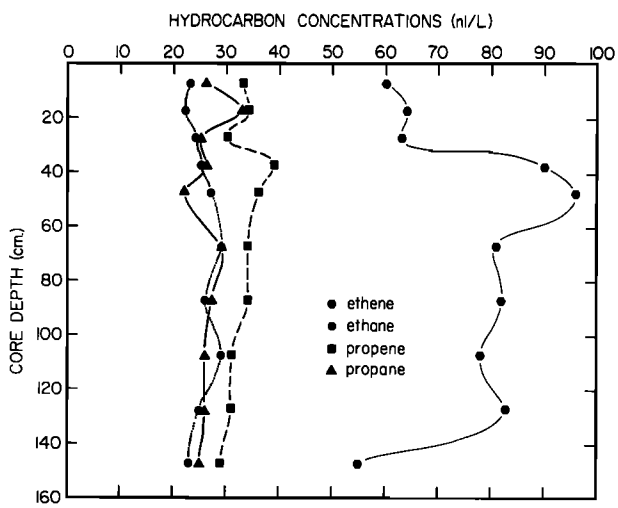


Fig. 6. Interstitial concentrations (nanoliters per liter pore water) of the C_2 and C_3 hydrocarbons with depth at station 6.

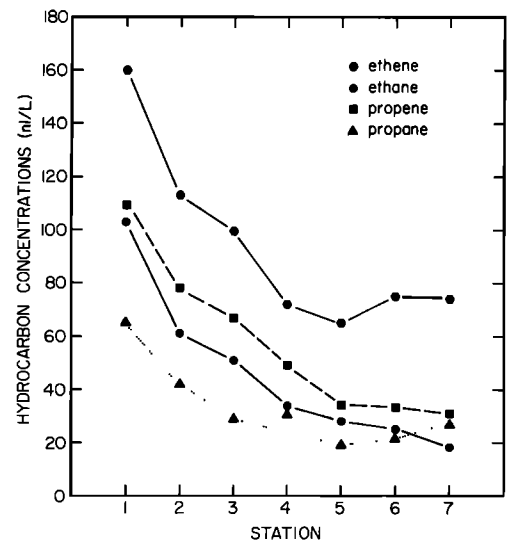


Fig. 7. Average concentrations (nanoliters per liter pore water) of the C_2 and C_3 hydrocarbons at stations 1–7.

the overlying water. These observations and conclusions are discussed in detail in another report [*Bernard,* 1978].

OTHER LIGHT HYDROCARBON PROFILES

Interstitial concentrations of ethene, ethane, propene, and propane at station 6 are plotted against sediment depth in Figure 6. These profiles are representative of the concentrations measured at the 12 stations and illustrate the behavior of the light hydrocarbons in the top 1.5 m of shelf sediment.

Ethene concentrations fluctuate with depth in the cores, whereas ethane, propene, and propane concentrations are relatively constant. Ethene levels are typically twice as high as those of the other gases, but no trends with sediment depth are observed. Figure 7 shows average concentrations of the four hydrocarbons at transect I stations. The average concentrations of each of the hydrocarbons are highest nearshore and decrease seaward until fairly uniform values are observed in the continental slope region (stations 5, 6, and 7). The average concentrations along transect II follow the same trend, although no samples were taken in the slope region for comparison.

The trends of the C_2 and C_3 hydrocarbons with distance from shore (Figure 7) are similar to the behavior of methane discussed previously. These patterns suggest that the concentrations of the C_2 and C_3 hydrocarbons in the top few meters of shelf and slope sediments are also supported by microbial activities. Microbial production of these gases was first demonstrated by *Davis and Squires* [1954]. As is true for methane, steady state concentrations of the C_2 and C_3 hydrocarbons must be controlled by biological oxidation and diffusion into the overlying water.

SUMMARY AND CONCLUSIONS

Concentrations of light hydrocarbons in the top few meters of Texas continental shelf and slope sediments are highest near shore and decrease regularly in an offshore direction. Vertical methane profiles exhibit maxima in the top 40 cm of sediment on the shelf, in contrast to downward increasing gradients in the slope region. Ethene concentrations fluctuate with depth in sediment cores but show no vertical trends. Ethane, propene, and propane concentrations are relatively constant with sediment depth throughout the cores, and average concentrations of the C_2-C_3 hydrocarbons decrease seaward to uniform levels in the slope region.

Methane is apparently microbially produced in microreducing environments and removed by biological oxidation and diffusion into the overlying water. Production rates are related to microbial activity, organic content, and temperature of the sediments. Profiles of C_2 and C_3 hydrocarbons imply that background concentrations of these gases are also controlled by microbial processes.

Further work needs to be done to substantiate the activity of methanogenic and other light-hydrocarbon-producing bacteria in sulfate-rich sediments. Interesting considerations include whether populations of methanogenic bacteria follow the general vertical microbial distributions and to what extent methane and other hydrocarbon gas would be produced in deep-sea sediments incubated at shallow water temperatures.

Acknowledgments. The authors wish to acknowledge the informative discussions on the microbiology of the Texas shelf with John Schwarz. Financial support for this work was provided by U.S. Bureau of Land Management contract AA550-CT7-11.

REFERENCES

Barnes, R. O., and E. D. Goldberg, Methane production and consumption in anoxic marine sediments, *Geology, 4,* 297–300, 1976.

Bernard, B. B., Kinetic modeling of interstitial methane, submitted to *Deep Sea Res.,* 1978.

Certes, A., Sur la culture, à l'abri des germes atmosphériques, des eaux et des sédiments rapports par les expéditions du Travailleur et du Talisman, *C. R. Acad. Sci., 98,* 690–693, 1884.

Claypool, G., and I. R. Kaplan, The origin and distribution of methane in marine sediments, in *Natural Gases in Marine Sediments,* edited by I. R. Kaplan, pp. 99–139, Plenum, New York, 1974.

Davis, J. B., and R. M. Squires, Detection of microbially produced gaseous hydrocarbons other than methane, *Science, 119,* 381–382, 1954.

Drew, G. H., Report of investigations on marine bacteria carried on at Andros Island, Bahamas, British West Indies, in May, 1912, *Carnegie Inst. Wash. Yearb., 1,* 136, 1912.

Emery, K. O., and D. Hoggan, Gases in marine sediments, *Amer. Ass. Petrol. Geol. Bull., 42,* 2174–2188, 1958.

Kaplan, I. R., and S. C. Rittenburg, Basin sedimentation and diagenesis, in *The Sea: The Earth Beneath the Sea, History,* vol. 3, edited by M. N. Hill, pp. 583–619, John Wiley, New York, 1963.

Lloyd, B., Muds of the Clyde Sea area, II, Bacterial content, *J. Mar. Biol. Ass., 17,* 751–765, 1931.

Martens, C. S., and R. A. Berner, Methane production in the interstitial waters of sulfate depleted sediments, *Science, 185,* 1167–1169, 1974.

Martens, C. S., and R. A. Berner, Interstitial water chemistry of anoxic Long Island Sound sediments, 1, Dissolved gases, *Limnol. Oceanogr., 22,* 10–25, 1977.

McAuliffe, C., Solubility in water of paraffin, cycloparaffin, olefin, acetylene, cycloolefin,a nd aromatic hydrocarbons, *J. Phys. Chem., 70,* 1267–1275, 1966.

Reeburgh, W. S., Observations of gases in Chesapeake Bay sediments, *Limnol. Oceanogr., 14,* 368–375, 1969.

Reeburgh, W. S., Methane consumption in Cariaco Trench waters and sediments, *Earth Planet. Sci. Lett., 28,* 337–344, 1976.

Reeburgh, W. S., and D. T. Heggie, Depth distributions of gases in shallow water sediments, in *Natural Gases in Marine Sediments,* edited by I. R. Kaplan, pp. 27–45, Plenum, New York, 1974.

Reuszer, H. W., Marine bacteria and their role in the cycle of life in the sea, III, Distribution of bacteria in the ocean waters and muds about Cape Cod, *Biol. Bull., 65,* 480–497, 1933.

Russell, H. L., Untersuchungen uber im Golf von Neapel lebende Bakterien, *Z. Hyg., 2,* 165–206, 1892.

Sackett, W. M., J. M. Brooks, B. B. Bernard, and H. Abdel-Reheim, Selected water column measurements: Low-molecular-weight hydrocarbons, Environmental Studies, South Texas Outer Continental Shelf, Biology and Chemistry, report to the U.S. Bureau of Land Management, Univ. of Tex. Mar. Sci. Inst., Port Aransas, 1977.

Toerien, D. F., and W. H. J. Hattingh, Anaerobic digestion, I, The microbiology of anaerobic digestion, *Water Res., 3,* 385–416, 1969.

Vogel, A., *Quantitative Inorganic Analysis,* John Wiley, New York, 1968.

Whelan, T., Methane and carbon dioxide in coastal marsh sediments, in *Natural Gases in Marine Sediments,* edited by I. R. Kaplan, pp. 47–61, Plenum, New York, 1974.

Zobell, C. E., Changes produced by microorganisms in sediments after deposition, *J. Sediment. Petrology, 12,* 127–136, 1942.

Zobell, C. E., *Marine Microbiology,* 240 pp., Chronica Botanica, Waltham, Mass., 1946.

Zobell, C. E., and D. Q. Anderson, Vertical distribution of bacteria in marine sediments. *Amer. Ass. Petrol. Geol. Bull., 20,* 258–269, 1936.

(Received September 12, 1977;
revised February 10, 1978;
accepted February 21, 1978.)